

# Effects of the Molecular Weight and Concentration of Poly(vinyl alcohol) on Slot Die Coating

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**ABSTRACT:** An experimental study was carried out to investigate the effects of the molecular weight and concentration of aqueous poly(vinyl alcohol) (PVA) solutions on the stable operating window of slot die coating. Various coating defects were observed outside the operating window. The window was found to expand with the PVA concentration and molecular weight increasing at low concentrations and to reach a maximum size at the gel point concentration, which corresponded to a critical Deborah number. Beyond this point, the effect of fluid elasticity became dominant, and the window began to shrink. This phenomenon was in contrast to that observed for low-mo-

lecular-weight glycerol solutions, in which the operating window was found to contract with the concentration or viscosity increasing. This anomalous behavior was attributed to the stretching or extension of long-chain PVA molecules, which effectively stabilized the fluid motion in the coating bead region. The maximum coating speed could be correlated with the PVA concentration and molecular weight in terms of the capillary number as a function of the dimensionless concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 654–662, 2010

**Key words:** coatings; gelation; processing; rheology

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is a common additive used in many coated products.<sup>1,2</sup> For example, it is a key ingredient for ink absorption in ink-jet media.<sup>3–5</sup> Because PVA is water-soluble, nontoxic, and easy to handle, it is also used extensively in coating research.<sup>6,7</sup>

The slot die coating method was invented by Beguin<sup>8</sup> and has been used extensively not only in the photographic industry but also in areas such as the manufacture of liquid-crystal display panels<sup>9</sup> and batteries.<sup>10</sup>

The analytical solution of slot die coating using the lubrication film theory was first presented by Ruschak,<sup>11</sup> who proposed the concept of an operating or coating window. The operating window defines the boundaries of stable and uniform coating, outside of which coating defects become noticeable. Higgins and Scriven<sup>12</sup> later extended the work of Ruschak by including the viscous effect in the coating bead region. More recently, Carvalho and Khesghi<sup>13</sup> applied the two-dimensional finite ele-

ment method to examine the operating window of slot die coating. Brethour<sup>14</sup> also studied the operating window theoretically using a commercial software package, FLOW 3D.

Lee et al.<sup>15</sup> experimentally investigated the operating coating window for slot die coating using a method similar to the slide coating employed by Gutoff and Kendrick.<sup>16</sup> They found that the functional dependence of the minimum wet thickness on the capillary number ( $Ca$ ), as predicted by Ruschak<sup>11</sup> and Higgins and Scriven,<sup>12</sup> was valid only in a low  $Ca$  range. The minimum wet thickness was found to be independent of  $Ca$  beyond a certain critical value of  $Ca$ . Later, Carvalho and Khesghi<sup>13</sup> reported that the minimum wet thickness could decrease at high values of  $Ca$ . The dependence of the minimum wet thickness on the Reynolds number in slot die coating was also experimentally presented by Chang et al.<sup>17</sup> Ning et al.<sup>18</sup> reported the effects of polymer additives on slot die coating behavior and found that a small amount of a polymer additive could effectively expand the operating window. Romero et al.<sup>19</sup> presented theoretical and experimental evidence on the effect of the extensional viscosity on the coating operation using several polymeric solutions. They predicted a smaller operating window as the extensional viscosity of the fluid increased. Recently, similar behavior was theoretically predicted with the Oldroyd-B and FENE-P models by Bajaj et al.<sup>20</sup> They expressed the growth of the operating window as a

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function of an elastocapillary number (the ratio of the Weissenberg number to  $Ca$ ), and they showed that the window narrowed as the liquid became more elastic. The effects of the addition of inorganic particles ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) to PVA solutions on slot die coating have also been reported (Chu and co-workers<sup>21,22</sup>). Other notable work on slot die coating can be found in several well-known textbooks.<sup>23,24</sup>

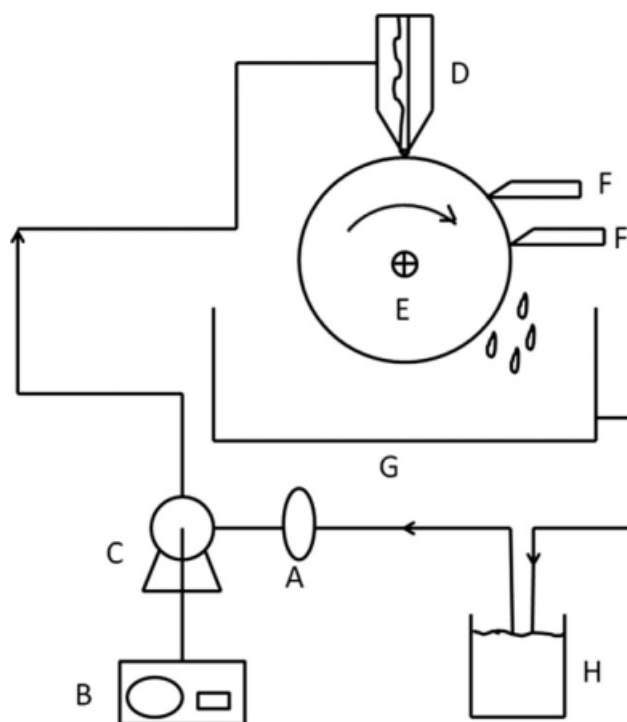
There are two difficulties in the simulation of slot die flow in the coating bead region. One is that the physics in the vicinity of the dynamic contact line of the upstream meniscus is not clear, and the other is that the downstream meniscus is not pinned on the slot die lip corner as previously assumed in theoretical studies.<sup>19,20</sup> Hence, a realistic criterion for the prediction of the onset of flow instability for polymer solutions in slot coating must be established experimentally.

In this study, the effects of the molecular weight and concentration of PVA on the operating window of slot die coating were experimentally investigated. Comparisons were made with the coating behavior of glycerol solutions of the same viscosity and surface tension. The effect of the fluid elasticity on the operating windows was also examined.

## EXPERIMENTAL

### Materials and physical property measurements

Two different grades of PVA were used as test solutions. Concentrated PVA solutions (20 wt %), called BP04 and BP24, were supplied by Chang-Chun Chemical Co. (Hsinchu, Taiwan). The molecular weights of BP04 and BP24 were 18,000 and 120,000, respectively. The polydispersity index of both grades was around 2. They also had the same degree of hydrolysis (i.e., the ratio of acetate groups to hydroxyl groups) of 86–89%. Coating PVA solutions of the desired concentration were prepared by the dilution of the stock solution with deionized water. Pure glycerol solutions, purchased from Riedel-de Haen (Seelze, Germany), were also diluted with deionized water. Rheological data, including the steady shear viscosity and dynamic moduli, were measured at room temperature with an ARES LS-1 (New Castle, DE) cone and plate rheometer over a shear rate range of 1–2000  $\text{s}^{-1}$  and a frequency range of 0.1–400 rad/s. The values of the surface tension and density of the coating solutions were determined with a surface tensiometer (CBVP-A3, Kyowa Interface Science Co., Ltd., Saitama, Japan) and a hydrometer, respectively. A surfactant (FSO, Du Pont, Wilmington, DE) was added to the coating solutions to adjust the surface tension. For comparison, several glycerol solutions of viscosities similar to those of the PVA solutions were also prepared for the coating experiment.

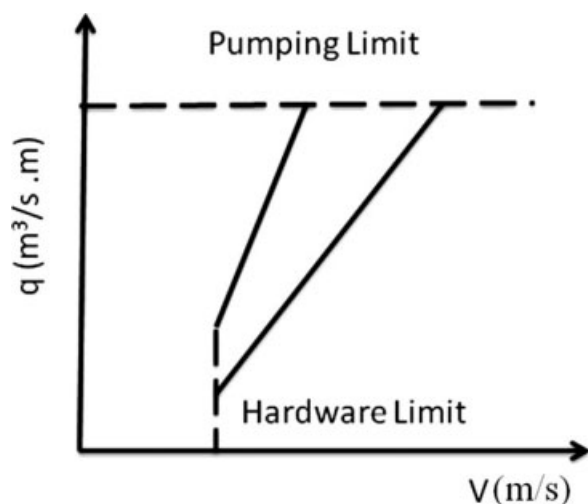


**Figure 1** Schematic of the experimental setup: (A) filter, (B) control panel, (C) pump, (D) slot die, (E) roller, (F,F') squeegees, (G) collecting tray, and (H) fluid tank.

### Coating flow experiment

The coating flow experiment was performed on a laboratory coater, as shown in Figure 1. The coating solution was fed into the slot die with a screw pump (4NE-20PM, Heishin, Kobe, Japan). The slot die was carefully designed with two internal distributing manifolds so that the liquid sheet emanating from the slot die exit would be uniform. The flow rate was regulated so that the liquid issuing from the slot die would create a thin, uniform liquid layer on the chrome-plated moving roller for observation. The coated solution was removed with two squeegees and returned to the reservoir for recycling.

The method of determining the operating windows of PVA was identical to that described in previous studies.<sup>15,16</sup> The slot gap and coating gap between the die lip and the roller surface were set at the same value,  $2.0 \times 10^{-4}$  m, throughout the entire coating experiment. The slot die was positioned vertically above the roller so that the coating solution emanating from the die would be impinged downward onto the roller surface at  $90^\circ$ . In each coating experimental run, the liquid flow rate was fixed initially at a very low value, and the corresponding lower and upper roller speed limits were determined. These speeds defined the lower and upper boundaries of the operating coating window. The roller speed was adjusted back and forth until a uniform coating film was established. The flow rate was



**Figure 2** Experimentally obtained operating window with the volumetric flow rate per unit coating width [ $q$  ( $\text{m}^3/\text{s} \cdot \text{m}$ )] versus the coating speed [ $V$  ( $\text{m}/\text{s}$ )].

increased slightly if no uniform flow could be obtained. The experiment was repeated by increases in the flow rate step by step to an upper flow rate limit beyond which no uniform coating was possible. The corresponding lower and upper roller speeds were recorded for each flow rate. The results were used to construct the operating window with flow rate vs coating speed. The region bounded within the window represented good-quality coating. The determination of the operating window was based on visual observation and inspection. Because the coating strip was only 10 cm wide, coating defects such as dripping, ribbing, air entrainment, and break lines could be clearly identified. The boundary between good and bad coatings was examined carefully by adjustments of the coating speed back and forth in the neighborhood of the critical speed. A schematic representation of an operating window is shown in Figure 2. Theoretically, a closed operating window should be obtained. However, because of the mechanical limitations of the pump and the roller speed, it was not always possible to obtain a closed window at the upper and lower ends.

## RESULTS AND DISCUSSION

### Rheology and other solution properties

The physical properties of the test solutions, including the density, surface tension, shear viscosity, and dynamic moduli, were determined before the coating flow experiment. There is very little variation in the fluid densities over the concentration ranges of the PVA solutions, and their values are only slightly above that of water, as shown in Tables I and II. Also shown in the tables are the surface tension and viscosity for the two grades of PVA solutions at different concentrations. For the low-molecular-weight PVA (BP04), the surface tension increases marginally with increasing polymer concentration, whereas it decreases with increasing concentration for the high-molecular-weight PVA (BP24). This is not unexpected because PVA is an active surface agent, and its effect on surface tension is much greater for solutions containing larger polymer molecules.

The steady shear viscosity and dynamic properties were determined for all test solutions at various room temperatures. As expected, the viscosity increases markedly with increasing polymer concentration for both PVA systems, especially those solutions with high polymer concentrations. As shown in the viscosity plot in Figure 3, most test solutions behaved as Newtonian liquids over the measured shear rate ranges, except for the highly concentrated solutions, in which a slight shear-thinning behavior was observed. Hence, only a single value of the viscosity, arbitrarily taken at a nominal shear rate of  $100 \text{ s}^{-1}$ , is quoted for each test solution in the tables. The apparent shear rate range in this slot coating system is between 100 and  $1000 \text{ s}^{-1}$ . Figure 3 shows plots of the steady-shear viscosity as a function of the shear rate for the two grades of PVA solutions over the shear rate range of  $1\text{--}2000 \text{ s}^{-1}$ ; the closed and open symbols represent the results for BP04 and BP24, respectively. The low-molecular-weight PVA (BP04) solutions behave as Newtonian liquids over the measured shear rate range until the concentration reaches 18%, at which a slight shear-thinning behavior at shear rate over  $800 \text{ s}^{-1}$  is noticeable. On the other hand, the shear-thinning behavior occurs at a much lower polymer concentration for the high-

**TABLE I**  
Physical Properties of BP04 at Different Concentrations

Concentration of PVA in solution (wt %)	Experimental temperature ( $^{\circ}\text{C}$ )	Fluid density ( $\text{kg}/\text{m}^3$ )	Surface tension ( $\text{mN}/\text{m}$ )	Fluid viscosity ( $\text{mPa} \cdot \text{s}$ )
14	21.5	1018	38.0	39
15	23.0	1021	38.1	100
16	22.9	1025	37.4	140
17	23.7	1027	37.8	180
18	23.4	1030	37.8	320

TABLE II  
Physical Properties of BP24 at Different Concentrations

Concentration of PVA in solution (wt %)	Experimental temperature (°C)	Fluid density (kg/m <sup>3</sup> )	Surface tension (mN/m)	Fluid viscosity (mPa s)
4	26.1	1009	38.6	46
5	25.5	1011	37.2	110
6	25.8	1015	35.9	220
7	24.9	1017	35.1	450
8	25.3	1020	34.3	860

molecular-weight PVA (BP24) solutions, that is, around 6 wt %.

The effect of the molecular weight  $M_v$  on the polymer solution viscosity is related to the intrinsic viscosity ( $[\eta]$ ) of the polymer. Because the concentration ranges of the two grades of PVA solutions were relatively high, it was not possible to obtain accurate  $[\eta]$  values experimentally by extrapolation. Instead, they were estimated with the Mark-Houwink equation:

$$[\eta] = KM_v^\alpha \quad (1)$$

The values of the Mark-Houwink parameters  $K$  (0.02 and 0.30 mL/g for BP04 and BP24, respectively) and  $\alpha$  (0.76 and 0.50 for BP04 and BP24, respectively) were taken from the literature.<sup>25</sup> The estimated  $[\eta]$  values are 0.0343 m<sup>3</sup>/kg for BP04 and 0.1039 m<sup>3</sup>/kg for BP24. Figure 4 shows a logarithmic plot of the specific viscosity versus the dimensionless concentration ( $[\eta]c$ ) for the two PVAs of different molecular weights in water. It is well known<sup>26</sup> that plotting the viscosity-concentration data in this manner will yield a master curve for the many polymer homologues of different molecular weights, and the slope at different sections of the curve defines the concentration regimes. Generally, the slope of

the curve obeys the following trends: (1) a slope of unity for dilute solutions, (2) a slope between 1 and 3.4 for semidilute solutions, and (3) a slope greater than 3.4 for concentrated solutions.

Figure 4 shows that the two sets of data do not quite fall onto a master curve. The slope of the BP04 line is higher than that of the BP24 line. The discrepancy is most likely due to the strong viscosity dependence on temperature. Although all rheological data were taken at room temperature, the viscosity of each coating solution was measured on a different day when the coating experiment was performed. As shown in Tables I and II, the average ambient temperature when the viscosity of the BP24 solutions was measured was about 2° higher than that for the BP04 solutions. If the viscosity dependence on the temperature was ignored and all data were least-square fitted into a straight line, then the slope of the line was approximately 4.5. This value of the slope agrees exactly with the results obtained for aqueous solutions of concentrated poly(ethylene glycol) and glycerol.<sup>26</sup>

According to de Gennes,<sup>27</sup> the upper limit of the dilute solution regime, which defines the critical concentration ( $c^*$ ), is obtained at  $[\eta]c^* \cong 1$ . Hence, the corresponding values of  $c^*$  are approximately 1 and 3 wt % for the aqueous BP24 and BP04 PVA solutions, respectively. Because the concentration ranges of the PVA solutions used in this study were

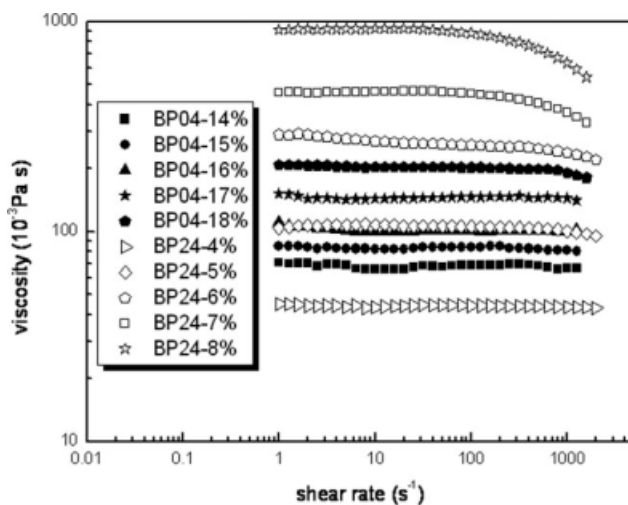


Figure 3 Viscosity as a function of the shear rate for BP04 and BP24 at different concentrations.

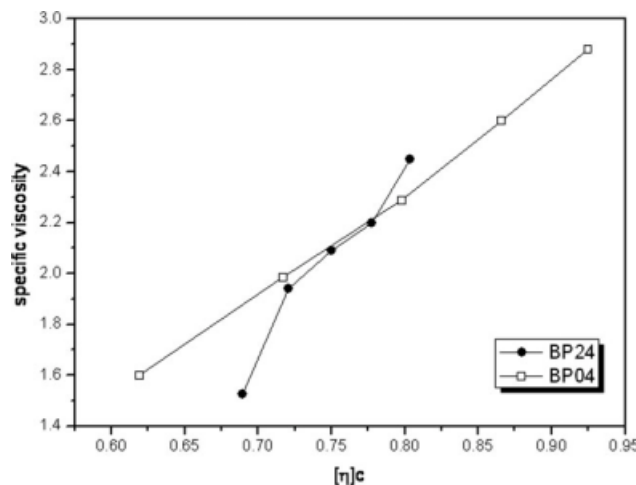
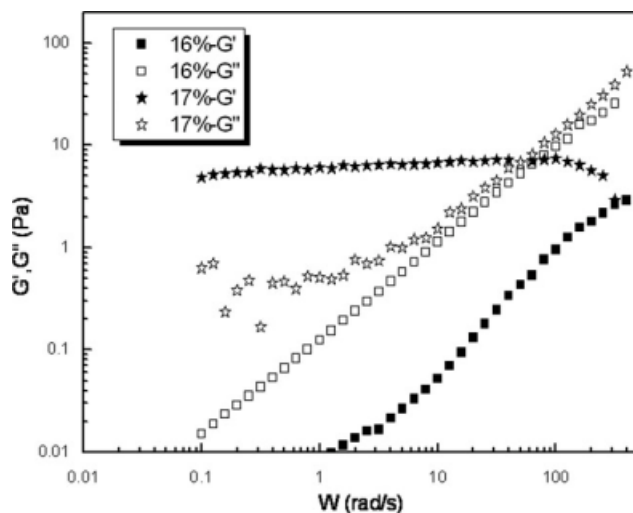


Figure 4 Specific viscosity as a function of  $[\eta]c$  for BP04 and BP24 solutions.

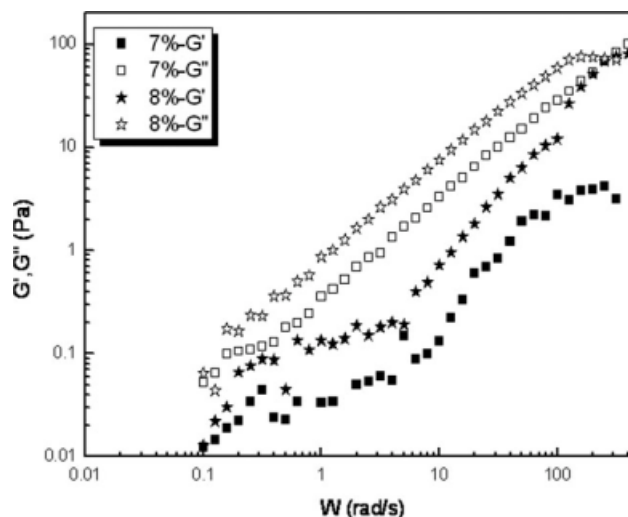




**Figure 5** Values of  $G'$  and  $G''$  as a function of  $\omega$  for 16 and 17% BP04 solutions.

much higher than  $c^*$ , most of the test solutions were in the semidilute or concentrated regime.

Because of the difficulties in obtaining the elastic properties of low-molecular-weight polymer solutions with the ARES-LS1 rheometer, oscillatory shear moduli could be measured only for the more concentrated PVA solutions. Figure 5 shows the results of the dynamic frequency sweep tests for the 16 and 17% BP04 solutions. The data are more scattered in the low frequency region because of instrumental limitations and noise. Values of the elastic modulus for the 16% BP04 solution are at least an order of magnitude smaller than the viscous modulus over the entire measurable frequency range. According to the de Gennes criterion, this solution should fall in the concentrated regime, in which polymer molecular chain entanglements would be expected. However, the elastic characteristic of this solution is not prominent from the dynamic shear measurements because of the relatively low molecular weight and size of PVA. For the 17% BP04 solution, a crossover of the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) curves occurs at a frequency around 60 rad/s, beyond which  $G'$  is greater than  $G''$ , and fluid elasticity becomes significant. In this context, the concentration of the PVA solution at which a crossover of  $G'$  and  $G''$  occurs over the measured frequency range is defined as the gel point concentration. Similar frequency sweep plots for the 7 and 8% BP24 solutions are shown in Figure 6. Once again, a crossover of the modulus curves was observed only for the higher concentration solution (8% BP24) at a sweeping frequency ( $\omega$ ) of 200 rad/s. A further increase in the PVA concentration would have produced a crossover point at a much lower frequency, resulting in a higher relaxation time. In other words, with increasing polymer concentration, a solution changes



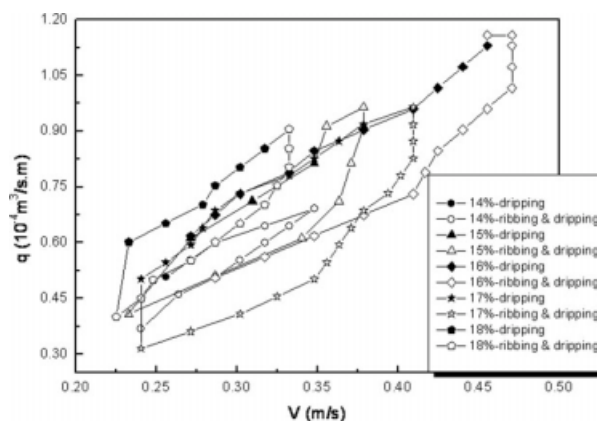
**Figure 6** Values of  $G'$  and  $G''$  as a function of  $\omega$  for 7 and 8% BP24 solutions.

from liquid-like behavior to gel-like behavior with increasing polymer chain entanglement.

## Coating flow results

### Operating windows of PVA solutions

The operating windows obtained for various BP04 solutions are presented in Figure 7. For the low-molecular-weight PVA solutions, two kinds of coating defects were observed outside the operating windows, that is, dripping and ribbing. Dripping refers to the coating defect when the solution is being pulled by gravity and falls below the coating bead region and normally appears at the low coating speed boundary. Ribbing refers to the lateral, wavy coating film surface caused by flow instability and usually occurs at the high coating speed boundary. In contrast to Newtonian liquids, in which the operating window has been found to contract with



**Figure 7** Operating windows of BP04 at different concentrations.

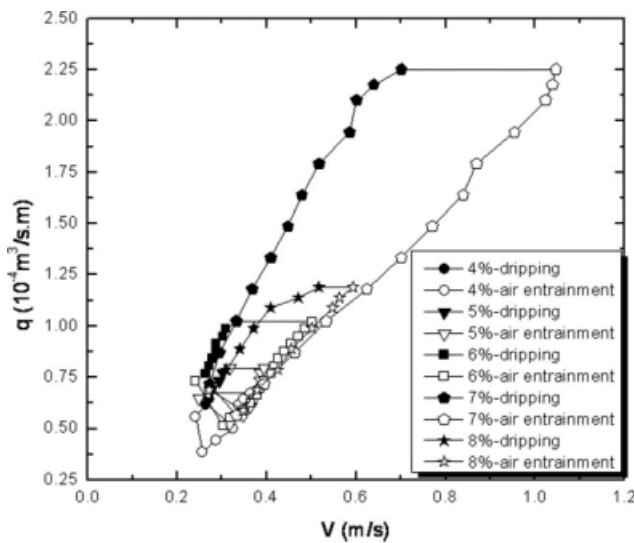


Figure 8 Operating windows of BP24 at different concentrations.

increasing liquid viscosity,<sup>15</sup> the window obtained for the BP04 solution actually expanded with increasing PVA concentration or viscosity until a transition concentration of around 16% PVA was reached. The opposite trend was observed beyond this transition concentration. This transition concentration (16%) is very close to the gel point concentration, at which  $G'$  is less than  $G''$  or fluid elasticity becomes significant. Below the gel point concentration, polymer molecules could still be stretched but not necessary entangled in the coating bead region because of the low polymer concentration. It appears that in polymer coating flow, viscous and surface tension forces are not the only dominant forces in determining the size of the operating window. It is likely that the stretching of polymer macromolecules is able to stabilize the flow in the free-surface region of the coating bead, thus delaying the onset of flow instability. When the solution concentration approaches the gel point concentration, polymer molecules are more densely packed, and fluid elasticity becomes a dominant force in the flow field. Therefore, a further increase in the PVA concentration beyond the gel point concentration results in a narrowing of the operating window. These findings are consistent with the theoretical predictions reported in the literature,<sup>19,20</sup> in which viscoelastic fluids have been shown to destabilize the coating flow at high Weissenberg or elastocapillary numbers.

The coating behavior for the high-molecular-weight BP24 solutions is similar to that for the BP04 solutions. As shown in Figure 8, the operating window expands initially with increasing PVA concentration, reaches a maximum just before the gel point concentration, and then contracts again with a further increase in the concentration. The maximum

operating window for the BP24 solution occurs at a concentration around 7%. The coating defect (dripping) observed at the low coating speed region is also similar to that of the BP04 solutions. However, air entrainment is observed at high coating speeds instead of ribbing. It occurs when the dynamic contact angle between the upstream meniscus and the moving substrate reaches 180°, and this facilitates the entrainment of air bubbles into the liquid stream.<sup>15,17</sup>

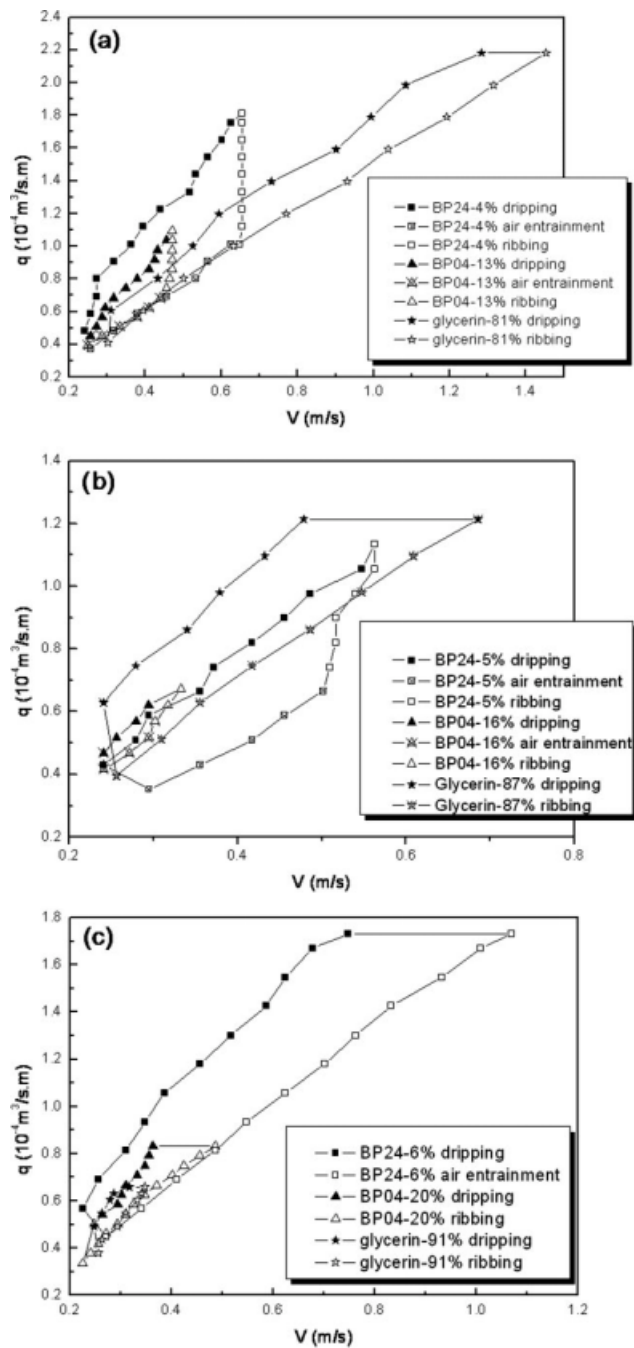


Figure 9 Comparison of the operating windows of glycerin and PVA solutions with fluid viscosities around (a) 0.05, (b) 0.1, and (c) 0.3 Pa.s.

TABLE III  
Physical Properties of Glycerol and PVA Solutions

Test solution	Concentration (wt %)	Experimental temperature (°C)	Fluid density (kg/m <sup>3</sup> )	Surface tension (mN/m)	Fluid viscosity (mPa s)
BP-24	4	21.4	1008	19.0	44
BP-04	13	24.1	1015	19.5	60
Glycerol	81	25.9	1210	19.6	49
BP-24	5	21.4	1011	18.0	100
BP-04	16	23.6	1029	19.4	100
Glycerol	87	25.9	1230	20.2	92
BP-24	6	22.8	1013	18.0	300
BP-04	20	23.1	1050	19.4	300
Glycerol	91.5	21.5	1240	20.2	290

Comparison of the operating windows of PVA and glycerol solutions

To verify that for aqueous polymer solutions other rheological properties such as the fluid elasticity and elongational viscosity, in addition to the shear viscosity, also play an important role in determining the size of the operating window, similar coating experiments were carried out with glycerols with viscosity and surface tension levels similar to those of BP04 and BP24 PVA solutions. Three sets of operating windows obtained for these solutions are compared in Figure 9. The physical properties of the coating liquids used for comparison are listed in Table III. As much as possible, the concentrations of the three types of coating solution were deliberately adjusted to produce three sets of viscosity levels around 0.05, 0.10, and 0.30 Pa s. The surface tension of all test solutions was controlled to a similar level (between 0.018 and 0.020 N/m) with a surfactant additive (FSO).

The results in Figure 9(a) indicate that the operating window of the low-molecular-weight glycerol solution is much larger than the windows of both BP04 and BP24 solutions at the lowest viscosity level of 0.05 Pa s. When the viscosity increases to 0.10 Pa s, the operating window of the glycerol solution becomes smaller because of the viscosity effect, but the windows of BP04 and BP24 are much larger than those obtained for the lowest viscosity solutions, as shown in Figure 9(b). This suggests that the extensional viscosity of the polymer solution may be responsible for the expansion of the operating windows of PVA solutions because all three liquids exhibit similar values of viscosity and surface tension. Figure 9(c) shows that a further increase in the viscosity to 0.30 Pa s results in a significant expansion of the operating window of the BP24 solution versus that of the glycerol solution. However, the operating window of the BP04 solution is smaller than that obtained for the 0.10 Pa s solution, as shown in Figure 9(b). As indicated earlier, the concentration of the BP04 solution in Figure 9(c) has already

exceeded its gel point concentration, at which the effect of fluid elasticity is more dominant than the effect of shear viscosity in the complex coating bead region.

#### Dependence of the operating window (maximum coating speed) on the PVA concentration and molecular weight

The functional dependence of the operating window (maximum coating speed) on the PVA concentration and molecular weight is presented in dimensionless form as  $Ca$  versus  $[\eta]c$  in Figure 10 for all PVA test solutions below their gel points. A master curve resulted in this dimensionless plot, in which  $Ca$  increases with the concentration and  $[\eta]$  or molecular weight increasing, and it attains a maximum just before the respective gel point concentration is reached, beyond which the maximum coating speed begins to fall until the flow is no longer stable. Because  $[\eta]$  is directly related to the polymer molecular weight, as shown by the Mark-Houwink equation [eq. (1)], an increase in the molecular weight

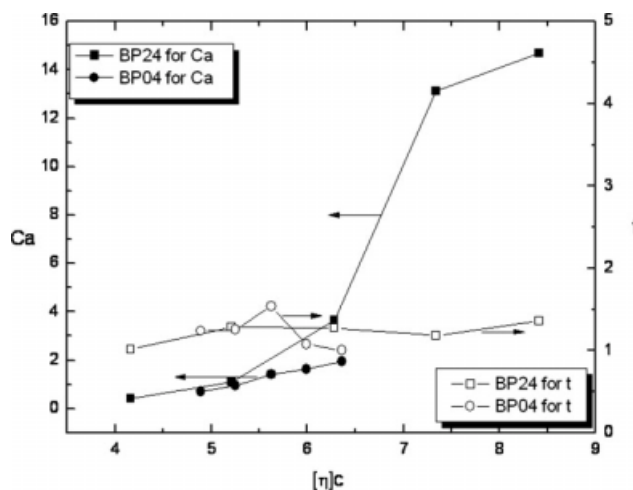


Figure 10 Capillary number ( $Ca$ ) and dimensionless film thickness ( $t$ ) versus  $[\eta]c$  for BP04 and BP24 solutions.

results in an increase in the maximum coating speed as long as the concentration is below its gel point. Also shown in the figure is the dimensionless plot of the minimum film thickness against  $[\eta]c$ . It is interesting to observe that despite the strong dependence of the operating window (maximum coating speed) on the PVA concentration and molecular weight, the minimum film thickness has an average value of 1.3 and is almost independent of  $[\eta]c$ , regardless of the individual values of the PVA concentration or molecular weight.

In complex flow situations such as the free surface flow of a liquid from a slot die onto a moving substrate, a dimensionless number called the Deborah number ( $De$ ) or Weissenberg number has normally been used to characterize the importance of elasticity in a given flow situation.  $De$  is defined as follows<sup>26</sup>:

$$De = \lambda/t_r \quad (2)$$

where  $\lambda$  is a characteristic (relaxation) time associated with the fluid elasticity and  $t_r$  is the residence time of the flow or contact time. The contact time is commonly taken as the inverse of the wall shear rate. When  $De \ll 1$ , then the elastic forces are negligible in comparison with the viscous forces.

Because the flow in the coating bead region is nonrectilinear and unsteady,  $De$  can be approximately defined by

$$De = \lambda(V_{ave}/L) \quad (3)$$

where  $V_{ave} = (V_f + V_s)/2$  is the arithmetic average velocity of the fluid velocity exiting from the die ( $V_f$ ) and the speed of the roller substrate ( $V_s$ ) and  $L$  is the length of the coating bead. If we assume that the fluid behavior follows a Maxwell model,  $\lambda$  is then equal to the reciprocal of the frequency of the crossover point (gel point) of  $G'$  and  $G''$  curves. As mentioned earlier, the size of the operating window is drastically reduced when the coating solution approaches its gel point concentration, that is, a 17% BP04 solution or an 8% BP24 solution. The  $\lambda$  values for the 17% BP04 and 8% BP24 solutions are about 0.0167 and 0.004 s, respectively, and the corresponding  $De$  values for the two PVA solutions are 11.48 and 3.56. Both values of  $De$  exceed unity, and this indicates the significance of elastic effects. In the current study, the crossover point of  $G'$  and  $G''$  could not be obtained experimentally within the measured frequency range for PVA solutions of less than 17 (BP04) or 8% (BP24). It is expected that the relaxation times for lower concentration solutions will be much shorter than 0.017 (17% BP04) or 0.004 s (8% BP24), and this will result in much smaller values of  $De$  under the same flow conditions, in which elastic

contribution may be neglected. Although in this study it was not possible to measure the extensional viscosity of the aqueous PVA solutions, it is believed that the expansion of the operating window in the lower concentration range is influenced by this important rheological property. Further work to quantify the effect of the extensional viscosity on the operating window may be necessary.

## CONCLUSIONS

The operating windows in the slot die coating of aqueous solutions of PVAs of different concentrations and molecular weights were experimentally investigated. The operating window was found to expand with increasing PVA concentration and molecular weight until the solution approached its gel point concentration, beyond which the window began to contract. This anomalous behavior was in contrast to that observed for Newtonian glycerol solutions, for which the operating window was found to narrow with increasing fluid viscosity or concentration.

The expansion of the operating window observed for the lower concentration PVA solutions could be attributed to the extension of polymer molecules into the coating bead region, which would enhance flow stabilization. Beyond the gel point concentration, sufficient molecular overlapping and entanglements exist, and the elastic force becomes the dominant force in controlling the maximum coating speed, as indicated by the magnitude of  $De$ . The dependence of the maximum coating speed and minimum film thickness on the PVA concentration and molecular weight have been presented in terms of  $Ca$  and the dimensionless film thickness as a function of  $[\eta]c$ .

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